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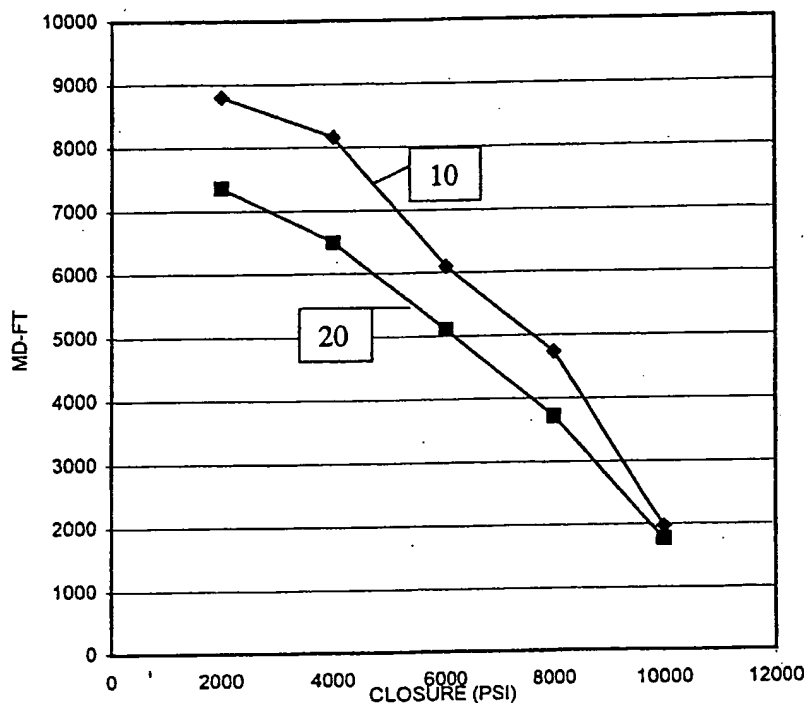
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(54) Title: PROPPANT COMPOSITION FOR GAS AND OIL-WELL FRACTURING



(57) Abstract: An aluminosilicate ceramic, spherical pellet made from spent ceramic catalyst. More specifically, a spherical ceramic pellet made from spent fluid cracking catalyst. The pellets can be made by grinding the catalyst particles, forming them into spherical pellets, and then sintering the pellets. The final product is useful as a proppant in oil and gas well fracturing.

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## PROPPANT COMPOSITION FOR GAS AND OIL WELL FRACTURING

### FIELD OF THE INVENTION

5           The present invention relates to proppant pellets prepared by using alumina-silica containing waste materials from industrial processes. The proppant pellets may be resin coated. The present invention further relates to a method for the manufacture of proppant pellets.

### 10           BACKGROUND OF THE INVENTION

In the completion and operation of oil wells, gas wells, water wells, and similar boreholes, it frequently is desirable to alter the producing characteristics of the formation by treating the well. Many such treatments involve the use of particulate material. For example, in hydraulic fracturing, particles called  
15   proppants are used to maintain the fracture in a propped condition. In hydraulic fracturing, proppant particles under high closure stress tend to fragment and disintegrate. At closure stresses above about 5,000 psi, silica sand, the most common proppant, is not normally employed due to its propensity to disintegrate. The resulting fines from this disintegration migrate and plug the interstitial flow  
20   passages in the propped interval. These migratory fines drastically reduce the permeability of the propped fracture. Since closure stress varies directly with depth, this means that sand is not a useful proppant material at depths greater than about 5,000 feet.

Sintered bauxite or high grade alumina have been used as proppant materials  
25   at well depths greater than 20,000 feet, but these high strength proppants have much higher densities than sand and therefore require high viscosity pumping fluids or high pumping rates. Larger pumping equipment is required, and wear rates on fluid carrying equipment is accelerated. In addition, the raw materials used to make the proppant materials are more costly.

30   Proppants of intermediate density are known, and work well in the intermediate depths and pressures, i.e., 7,000 to 14,000 feet (5,000 - 10,000 psi).

resin/outer resin boundary, as described in U.S. Pat. No. 5,422,183 assigned to Santrol, Inc, incorporated herein by reference as if fully written out below.

### SUMMARY OF THE INVENTION

- 5           The present invention utilizes spent ceramic media from petroleum refining operations, where the media provides a catalytic function during "cracking" of the hydrocarbons, while drawing out impurities from the crude oil as it passes through a packed column of ceramic beads. These beads are manufactured by Englehard Corporation, WR Grace and Akzo Nobel as well as other Far Eastern producers and  
10       are variously known as fluid cracking catalyst, e-cats, and equilibrium catalyst (hereinafter referred to as "fluid cracking catalyst" or "FCC"). The use of catalytic ceramic media for removing impurities from petroleum products is a long established art. The catalytic media can be regenerated after use as a cracking catalyst several times but eventually is spent, and is discarded as waste material.
- 15       The present invention uses the FCC as a base material for remanufacturing larger ceramic spheres, which can be used in the hydraulic fracturing of subterranean oil and gas bearing formations.

          The present invention provides a spherical ceramic proppant pellet comprising spent fluid cracking catalyst particles, wherein the pellet is formed by  
20       reducing the median particle size of the catalyst; mixing the catalyst particles with water and a binder to form spherical pellets; and sintering the pellets.

          The present invention also provides a method for preparing a spherical ceramic proppant pellet, the method comprising the steps of providing spent fluid cracking catalyst particles; reducing the particle size of the catalyst particles; mixing  
25       the catalyst particles with water and a binder to form spherical pellets; and sintering the pellets.

          The present invention further provides a proppant composition comprising spent fluid cracking catalyst, wherein the spent fluid cracking catalyst comprises from about 25 to about 80 weight percent synthetic silica, and from about 20 to

zeolites also contain counterions such as sodium, and ammonium ions. Zeolites employed in the manufacture of the FCC catalyst are synthetic versions of naturally occurring zeolites called faujasites. Zeolites with applications to FCC are Type X, Type Y, and ZSM-5. Both X and Y zeolites have essentially the same crystalline structure. The major difference is that the X zeolite has a lower silica/alumina ratio than the Y zeolite. Virtually all of today's catalysts contain Y zeolite or variations thereof. One variation is an aluminum-deficient zeolite, called ultrastable Y, or simply USY. Zeolites are sometimes ion exchanged with rare earth components in order to increase catalytic activity and thermal stability. Rare earth is a generic name for fourteen metallic elements of the lanthanide series, including lanthanum and cerium.

The matrix component of the FCC can also have catalytic activity. Alumina is normally the source for the matrix component. Most FCCs contain an amorphous alumina matrix, but some catalyst suppliers incorporate a form of alumina that has a crystalline structure.

The filler component is a clay incorporated into the catalyst to dilute its activity. Kaolin  $[Al_2(OH)_2, Si_2O_5]$  is the most common clay used in the FCC catalyst. One FCC catalyst manufacturer used kaoline clay as a skeleton to grow the zeolite in situ.

The binder serves as a "glue" to hold the zeolite, matrix and filler together. The functions of the filler and the binder are to provide physical integrity and mechanical strength. They impact such characteristics of the FCC as density, attrition resistance, and particle size distribution.

Spent fluid cracking catalyst also contains a number of metal contaminants, including nickel, vanadium, iron, antimony and copper. These contaminants originate largely from the heavy, high-molecular weight fraction of the FCC feed. The quantity of these metals on the FCC is determined by their levels in the petroleum feedstock and the catalyst addition rate. Essentially, all these metals in the feed are deposited on the catalyst. Much of the iron on the FCC comes from metal scale from piping.

Table A

| Chemical Name                      | Wt Percent |
|------------------------------------|------------|
| Silica (synthetic), $\text{SiO}_2$ | 25-80      |
| Alumina $\text{Al}_2\text{O}_3$    | 20-75      |
| Quartz ( $\text{SiO}_2$ )          | <1.0       |
| Antimony                           | 0-2500ppm  |
| Copper                             | 5-1000ppm  |
| Vanadium                           | 45-7000ppm |
| Lead                               | 200ppm     |

This chemical analysis is included for example purposes only, and should not be considered as a limitation of the FCC used to produce the proppants of the present invention. In some instances, alumina or silica can be added, such as clay or silica gel, to adjust the silica:alumina weight ratio to 1:1 to 2:1.

The spherical ceramic proppant pellets of the present invention are prepared by a method comprising the steps of providing spent fluid cracking catalyst particles, reducing the particle size of the catalyst particles, mixing the catalyst particles with water and a binder to form spherical pellets, and sintering the pellets. The pellets are preferably screened to provide a suitable median particle size.

Reduction of the particle size of the FCC particles is preferably accomplished by conventional ball milling techniques, including either wet or dry ball milling. The median particle size of the FCC particles after reduction is preferably about 1 to about 10 microns, and more preferably about 2 to about 6 microns, as measured by laser diffraction.

The comminuted FCC particles are then mixed with water and a binder. Suitable binders include, but are not limited to, polyvinyl acetate, methyl cellulose, and polymethylmethacrylate. The amount of water used is preferably 25-45 percent by weight of fluid cracking catalyst, but will vary depending on the composition of the FCC. The amount of binder used is preferably about 0.1% to 0.5% by weight, preferably about 0.2 to 0.25%, but will depend on particle size distribution and shape.

Mixing may be accomplished by conventional methods. Preferably, a Eirich mixer is used, such as an Eirich RVO2. The pellet size is determined by mixer run time. A mix time of 45 seconds to 80 seconds is usually sufficient in the particular

°F for 1 hour. The specific gravity of the product at this stage was approximately 2.1gm/cm<sup>3</sup>.

After drying, the spherical pellets were sintered in a rotary kiln at a temperature of between 1,325 °C to 1,500 °C for about 30 minutes. After sintering, the pellets were screened to 20/40 mesh.

The pellets so formed are surprisingly similar in performance to existing ceramic proppant pellets, albeit with slightly lower crush resistance and lower conductivity with respect to brine and hydrocarbons, as shown in FIG. 1.

10. Conductivity Data

Conductivity testing to determine the relative conductivity of the final FCC pellets was followed according to standard StimLab procedures using 2% KCl as the flowing medium. As shown in Table 1, the data indicate that the FCC product, although slightly lower in absolute conductivity, is within 10% of the performance of a typical lightweight ceramic at higher closures (10,000 psi). This is graphically represented in FIG. 1, where line 10 shows the performance of commercial lightweight ceramic proppant, and line 20 show the performance of the FCC ceramic proppant.

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Additional proppant pellets were prepared from spent FCC catalyst according to the above described procedure, with 24 hour wet milling in a ball mill, drying and pressing into pellets. Sintering was conducted at 1300°C, 1400°C or 1500°C for 10 minutes. A final density of 99.6% of theoretical was achieved. X-ray diffraction indicated that the pellets contained about 50 to about 60 mol % cristobalite and about 40 to about 50 mol% mullite.

Other proppant pellets prepared according to the process of the present invention were tested for conductivity as described above, and the results of the tests are reported in Table 3, below.

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Table 3

| Closure (psi) | Conductivity (md-ft) |
|---------------|----------------------|
| 1000          | 8750-10278           |
| 2000          | 6500-7365            |
| 4000          | 5500-6500            |
| 6000          | 4800-5100            |
| 8000          | 3500-3719            |
| 10000         | 1650-1770            |

Advantageously, proppant pellets comprising spent fluid cracking catalyst utilize waste materials from the petroleum refining process which would otherwise be costly to dispose of or reclaim. The proppant pellets of the present invention are lightweight, low density materials with crush strength and conductivity approximating those of existing products.

The utility of the FCC ceramic proppant of the present invention can be extended into high stress applications by coating the proppant with a resin coating. The resin coating may be cured or curable. In one embodiment, the FCC ceramic proppant pellets are coated with a resin dissolved in a solvent which is then evaporated. The resin is then cured. In another embodiment, the FCC ceramic proppant pellets are mixed with a melted resin which is then cooled, coating the pellets. The resin coating is then cured. Alternately, the resin coating is curable, but not substantially cured prior to use. In this embodiment, the resin is cured after injection into the well formation by techniques known in the art.

the normal reaction conditions used for the formation of the phenol-formaldehyde resin. The coupling agent is added to the resin after the phenol formaldehyde condensation reaction has occurred and the resin has been dehydrated to the final free phenol and melt viscosity range.

5           A preferred resin of the inner coating is a phenolic novolac resin. Particularly suitable are phenolic novolac resins manufactured by Georgia Pacific, known as 99NO7, and by OxyChem, known as 24-715. The GP-099N07 resin has a softening point range of 85 °F-100 °F. The OxyChem 24-715 exhibits a softening point range of 70 °F-87 °F. When either resin is used, it is necessary to add to the  
10       mixture a cross-linking agent to effect the subsequent curing of the resin. Hexamethylenetetramine is the preferred material for this function as it serves as both a catalyst and a source of formaldehyde.

          The coupling agent to be employed is chosen based on the resin to be used. For phenolic resins, the coupling agents include amino, epoxy, and ureido organo  
15       silanes. Epoxy modified gamma-glycidoxypolytrimethoxysilane has given excellent results when used in the amount of 0.50 -1.00% based on the weight of the resin. The use of coupling agents as incorporated into the resin and as applied directly to the particulate substrate is discussed in Graham et al, U.S. Pat. No. 4,518,039, incorporated herein by reference as if fully written out below.

20           The outer coating of resin is formed from a heat curable resin coating formed over the inner resin. As stated previously, this outer resin must be curable at conditions that do not completely cure the inner coating thus leaving the inner coating curable. The preferred resins for the outer coating are of the resole type. Particularly suitable is a fast curing resole resin manufactured by Georgia Pacific  
25       known as 102N68. Resole resins generally are provided dissolved in a methanol and water solution as is Georgia Pacific 102N68. The resin exhibits an extremely fast cure having a 150 °C hot plate cure time of 30 seconds or less. The preferred resole should be in a solution of water and methanol as the solvent system. The organic solids level should be 65-75%, with a water content in the 5-15% level. The hot  
30       plate cure time at 150 °C should be in the range of 25-40 seconds.



Following this mixing step from about 5 to about 25%, by weight of the resin, of hexamethylenetetramine is added to the substrate resin mixture. The preferred amount of hexamethylenetetramine is about 13% by weight of the resin. After addition of the hexamethylenetetramine the entire mixture is allowed to mull  
5 for approximately one minute. Then water is added to quench the reaction of the inner resin coating. The amount of water added and the timing of its addition is adjusted to quench the curing of the inner resin while maintaining sufficient heat in the proppant to cure the outer coating that is added next.

The outer resin is then coated over the inner resin and allowed to  
10 substantially cure. Substantially cured, as used herein, is to be interpreted as meaning that the cross-linking reaction of the resin is substantially complete and that at typical downhole temperatures only minimal additional curing takes place. When the outer coating is the preferred resole, its addition is preferably carried out by adding it as a solution in a water/methanol mixture comprising between 15-30%  
15 methanol and 5-15% water. The preferred mixture is 6% water and 25% methanol.

As can be appreciated, it is useful in preparing the coated proppant of the present embodiment of the invention to precisely control the heat and mass balance to ensure that a cured outer coating encapsulates a still curable inner resin coating. One skilled in the art will recognize that batch size, equipment used, and resins  
20 selected will affect process conditions. Initial process temperature, process intervals, amounts of quench water added and amounts of solvent are all interrelated and may be manipulated to arrive at an optimal process. Although experimentation may be required, optimization is within the level of skill in the art.

In yet another preferred embodiment, the FCC ceramic proppant pellet is  
25 coated with a substantially cured inner resin coating and an outer resin coating which may be heat curable, fully cured, or of intermediate nature. A reinforcing agent may be interspersed at the inner resin coating/outer resin coating boundary. Suitable resins include those described above in the previous embodiment.

A key to the increased strength of the resin coated particles of this  
30 embodiment is the addition of a reinforcing agent in the boundary region between

corrosion inhibitors, cross linkers and the like, known in the art. Injection of the fluid is typically continued until a fracture of the desired geometry is obtained. Preferably the fracture at the well bore is at least 2.5 times the diameter of the largest proppant pellet. A carrier fluid having the proppant suspended therein is  
5 then pumped into the fracture. If the particles are resin coated with a curable resin, the temperature of the carrier fluid during pumping operations will be low so as to prevent premature curing of the outer resin coat. The carrier fluid bleeds off into the formation and deposits the proppant pellets in the fracture. The process is controlled by fluid loss agents which are small aggregate particles which temporarily  
10 slow the fluid loss to the formation.

After the proppant is placed, the well is shut in with pressure maintained on the formation. As the pressure within the fracture approaches the normal formation pressure, the fracture walls close in on the proppant and apply an overburden stress thereto. Deeper wells exert higher closure stress and require stronger proppants.  
15 Some curable resin coated proppants do not develop their full strength until the resin coating has cured in the formation. In the event of rapid closure of the fracture, the proppant could be crushed before the resin cures, resulting in decreased permeability.

When proppant pellets having an inner curable coating and an outer  
20 substantially cured coating are used, it is believed that the closure stress ruptures the outer coating exposing the curable inner coating. At the same time ambient formation temperature heats the inner resin coating. Initially, the resin fuses and unites at contact areas between contiguous particles or with the formation walls. As the temperature increases the polymerization reaction proceeds until the resin is  
25 cured into an insoluble and infusible crosslinked state. Grain to grain links are formed in pendular regions between adjacent particles and bond the packed particles into a permeable mass having considerable compressive strength.

## CLAIMS

What is claimed is:

1. A spherical ceramic proppant pellet comprising spent fluid cracking catalyst particles, wherein the pellet is formed by:
  - a. reducing the median particle size of the catalyst;
  - b. mixing the catalyst particles with water and a binder to form spherical pellets; and
  - c. sintering the pellets.
2. The proppant pellet of claim 1, wherein the pellet has a Krumbein roundness and sphericity of greater than or equal to 0.9.
3. The proppant pellet of claim 1, wherein the pellet has a crush strength at 7,500 psi of less than or equal to 9.1 percent.
4. The proppant pellet of claim 1, wherein the pellet has a conductivity at least about 1650 md-ft, after 50 hours at 10,000 psi and 250 °F using 2% KCl as the flowing medium.
5. The proppant pellet of claim 1, wherein the spent fluid cracking catalyst comprises from about 25 to about 80 weight percent silica, and from about 20 to about 75 weight percent alumina.
6. The proppant pellet of claim 1, wherein the pellet comprises silica and alumina in a weight ratio of about 2:1 to about 1:1.
7. The proppant pellet of claim 1, wherein the pellet comprises silica and alumina in a weight ratio of about 1:1.
8. The proppant pellet of claim 1, wherein the spent fluid cracking catalyst comprises a zeolite.

the outer resin coating may be cured or curable, and optionally a reinforcing agent.

18. The method of claim 11, wherein the spent fluid cracking catalyst particles comprise a zeolite.
- 5 19. The method of claim 11, further comprising screening the pellets to a mean particle size of 20/40 mesh.
20. A proppant pellet composition comprising pelletized and calcined spent fluid cracking catalyst, wherein the spent fluid cracking catalyst comprises from about 25 to about 80 weight percent silica, and from about 20 to about 75 weight percent alumina.
- 10 21. The proppant pellet composition of claim 20, wherein the silica and alumina are present in a weight ratio of silica/alumina of from about 2:1 to about 1:1.
22. The proppant pellet composition of claim 20, wherein the silica and alumina are present in a weight ratio of silica/alumina of about 1:1.
- 15 23. The proppant pellet composition of claim 20, wherein the density of the pellet composition after sintering is from about 2 g/cm<sup>3</sup> to about 2.7 g/cm<sup>3</sup>.
24. The proppant pellet composition of claim 20, wherein the mean particle size of the pellet composition is about 20/40 mesh.
25. The proppant pellet composition of claim 20, wherein the spent fluid cracking catalyst optionally further comprises at least one of:
- 20

up to about 1000 parts per million copper;

up to about 7000 parts per million vanadium;

up to about 200 parts per million lead;

up to about 7000 parts per million nickel;

30. A method of propping a fracture in a subterranean formation comprising creating a fracture in said subterranean formation, and placing in said fracture a quantity of the proppant pellets set forth in any one of the above claims.

## INTERNATIONAL SEARCH REPORT

International application No.  
PCT/US01/42184

## A. CLASSIFICATION OF SUBJECT MATTER

IPC(7) :C04B 35/18

US CL :501/127, 128, 133; 264/117

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 501/127, 128, 133; 264/117

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

EAST

SEARCH TERMS: PROPPANT, CATALYST, CERAMIC, ALUMINA, SILICA

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

| Category* | Citation of document, with indication, where appropriate, of the relevant passages | Relevant to claim No. |
|-----------|--|-----------------------|
| A         | US 4,879,181 A (FITZGIBBON) 07 November 1989, claims 1-14 in columns 12-14.        | 1-30                  |
| A         | US 4,427,068 A (FITZGIBBON) 24 January 1984, claims 1-6 in columns 13-14.          | 1-30                  |
| A         | US 4,944,905 A (GIBB ET AL.) 31 July 1990, see claims 1-12 in columns 11-12.       | 1-30                  |
| A         | US 4,668,645 A (KHAUND) 26 May 1987, claims 1-2 in columns 5-6.                    | 1-30                  |
| A         | US 4,440,866 A (LUNGHOFFER ET AL.) 03 April 1984, claims 1-9 in columns 8-10.      | 1-30                  |

☐ Further documents are listed in the continuation of Box C.
 ☐ See patent family annex.

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|-----|---|-----|--|
| "   | Special categories of cited documents:  | "I" | later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention  |
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| "O" | document referring to an oral disclosure, use, exhibition or other means  |     |  |
| "P" | document published prior to the international filing date but later than the priority date claimed  |     |  |

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